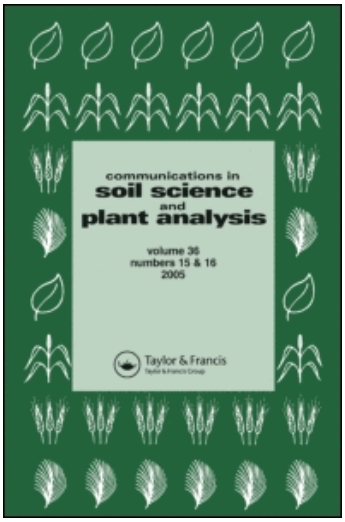

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Enzyme activities in appalachian soils: 1. Aryl-sulfatase

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ENZYME ACTIVITIES IN APPALACHIAN SOILS: 1. ARYL-SULFATASE

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ABSTRACT: Sulfatase enzymes in soil play an important role in transformation of organic forms of S into inorganic forms of plant available S. Arylsulfatase (AS) activities in fourteen hill land soils of the Appalachian region were assayed. Magnitude of AS activities were related to selected soil properties. The top two horizons from each of the soils were sampled during early spring, passed through a 2 mm sieve, and stored under field moist conditions at 4°C. Each soil type has its own level of AS activity. The average enzyme activities of surface samples were more than 2.4 times higher than those of subsurface horizons. The AS activities were positively correlated with organic C, N, forms of S and P, original soil moisture by weight and volume, and basic cations. Knowledge of the relationship between enzyme activities and soil properties should contribute to the development of fertility management systems for the hill-land soils of the Appalachian region.

INTRODUCTION

Many soils in the Appalachian region are under forest vegetation and have accumulated a considerable amount of organic matter in their surface horizons. The majority of the plant nutrients in these soils appear to be bound in organic forms. Essentially, all the sulfur in soils of humid regions are known to occur in organic forms (1). In many soils, organic forms of S comprise a large portion of the total S (1,2,3,4). Most of the organic sulfur in soils occurs in HI-reducible (sulfate ester-S) and C-bonded sulfur (e.g., cystine and methionine (1,2,4,5). In various soils of the world, the HI-reducible sulfur fraction amounts to 30 to 88% of the total organic S (1,4,6). Esters are known to be one of the more readily mineralizable forms of organic S in soil (4).

Sulfatase enzymes play an important role in transformation of organic S into inorganic S, which is subsequently made available for plant utilization (4,7,8,9). Arylsulfatase (arylsulfate sulfohydrolases, EC 3.1.6.1) are ubiquitous in soils and are known to catalyze the hydrolysis of an arylsulfate anion by fission of the O-S bond (10). Activities are known to decline with depth in agricultural soils (11), salt marshes (12) and peat (13). Arylsulfatase activity in different soils is significantly correlated with organic C (6,9,11). Tabatabai and Bremner (11) found no significant relation between arylsulfatase activity and percent N, clay, or sand content in 27 Iowa agricultural soils. However, in Tussock grassland soils, Speir (9) observed a significant correlation between arylsulfatase activity and soil moisture content and total N. The objectives of the present study were to measure arylsulfatase activities in the top two horizons of major hill land soils of Appalachia and to test for relationships between enzyme activities and selected soil properties.

MATERIALS AND METHODS

Soil and Soil Analysis: Fourteen major hill land soils of the Appalachian region were selected for this study. Figure 1 shows the distribution of these soils in the Appalachian region. Bulk samples from the top two horizons of each soil were collected in late spring, passed through a 2 mm sieve, and stored at 4°C in a field moist status.

The moisture content of soil samples at the end of incubation was determined by drying 48 h at 105°C. The percent water content was multiplied by bulk density to obtain volumetric water content. Bulk density was estimated by taking 60 mm soil cores of known volume. The percent water-filled porosity (%WFP) was estimated according to Linn and Doran (14). Soil pH was measured in water (1:1). Clay, sand, and silt were determined by pipette method. Exchangeable cations (15) and exchangeable H and Al (16) were also determined to obtain cation exchange capacity (CEC) and exchangeable bases (EB). Total C and N were determined using a Leco CHN 600 Analyzer. The soils were extracted with Bray-1 reagent (0.025 M HCl + 0.03 M NH_4F), and P in the extractant was detected by the color development method of Murphy and Riley as modified by Olsen and Summers (17). Organic P was determined by the ignition method of Olsen and Summers (17) and represents difference between total (ignited) and inorganic (unignited) P. Organic S was computed by taking the difference between total S determined by Leco

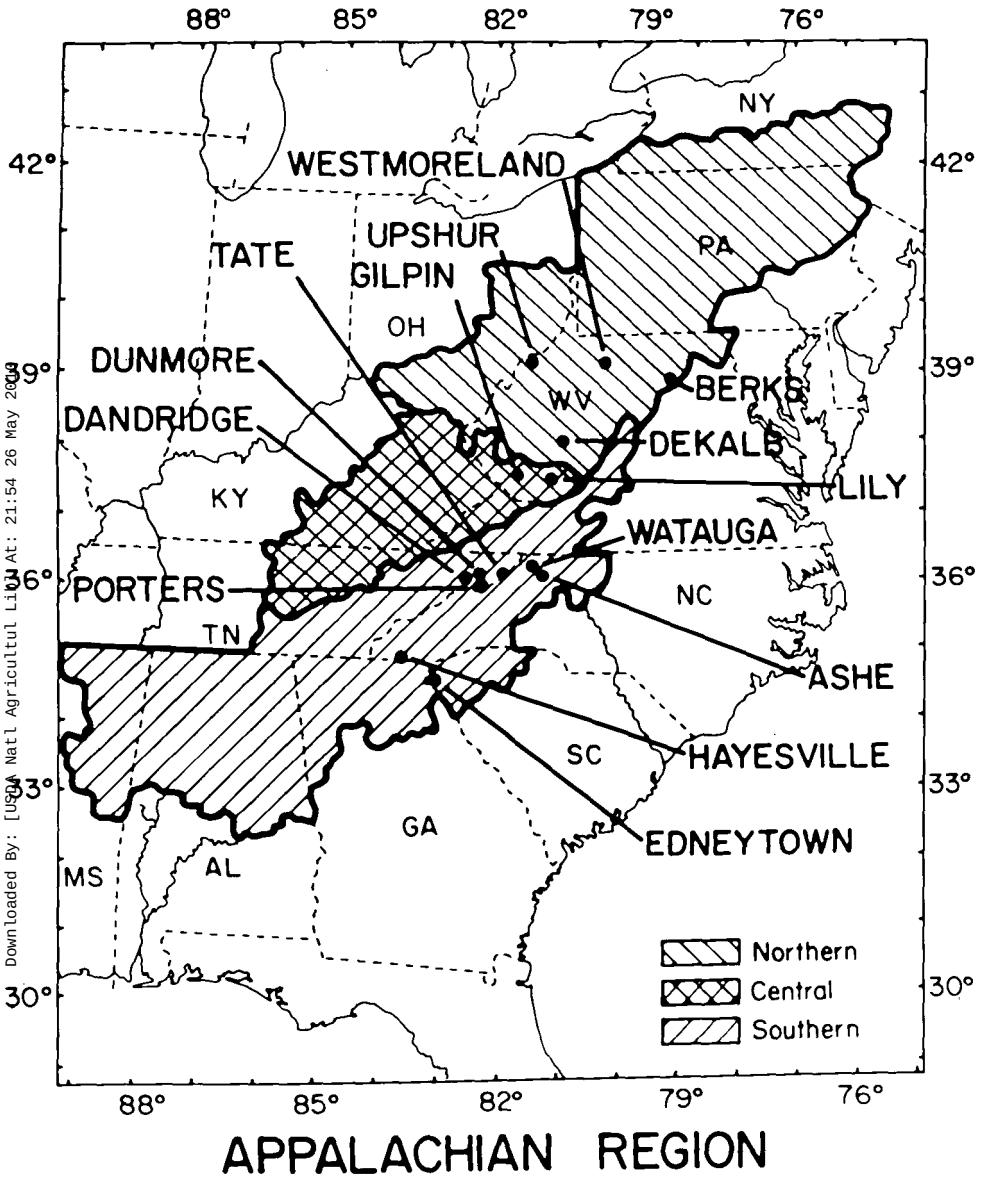

Figure 1. Collection sites for major hill land soils of the Appalachian Region.

Analyzer (Leco, SC 132, St. Joseph, MI)[a] and extractable S from the Bray extractant. Extractable S and cations of other extractants were determined by inductively coupled plasma emission spectroscopy (ICP). The selected soil properties of surface and subsurface horizons are presented in Table 1.

Assay of Arylsulfatase: Arylsulfatase (AS) activity in different soil horizons was assayed by the method of Tabatabai and Bremner (18) and Tabatabai (19), which involves colorimetric estimation of the p-nitrophenol released by incubation of soil with pH 5.8 buffered potassium p-nitrophenyl sulfate solution and toluene at 37°C for 1 hour. This method has been successfully used in detecting AS enzyme activities in various types of soils (5,6,11,12,13). The AS activities in all the soil samples were determined after 10 months of soil storage.

Statistical Method: The AS activities of different horizons were statistically analyzed by one-way ANOVA with separation of means by Duncan's Multiple Range Test. Simple correlation coefficients (r) between AS activities and soil properties were calculated.

RESULTS AND DISCUSSIONS

The arylsulfatase (AS) activities were different in different soils and were 2.4 times higher in surface than in subsurface horizons (Table 2). A decline in AS activities with soil depth in various ecosystems is well documented, and such a decline is often related to a reduction in soil organic C and moisture content (6,11,12). Association of enzymes with the humic polymers that are present in organic C of the soil offers the best form of protection for the enzymes from denaturation and biological degradation (20,21). Among surface samples, the Dandridge, Tate, and Gilpin soils had the highest AS activities, while Ashe and Edneytown soils had the lowest AS activities. Subsurface samples of Tate recorded the highest and Ashe, Watauga, and Edneytown recorded the lowest AS activities (Table 2). The variation in AS activities in soils has been related to soil texture, pH, moisture, forms of P and S, and CEC (4,9,11,22.23). Soils with low AS activities contained relatively low amounts of C, N, and organic P and S, thus, indicating that the organic matter content plays a fundamental role in estab-

[a]The use of trade names does not imply endorsement by the U.S. Department of Agriculture of the products names, nor criticism of similar ones not mentioned.

TABLE 1
Origin, Classification and Selected Properties of Soils Used

Soil Series	Classification	Horizon	Clay	pH H_2O	C	N	Sulfur		Phosphorus		CEC[a]
							Organic	Extract	Organic	Bray	
			g kg^{-1}		---g kg^{-1}---		----------mg kg^{-1}----------				
North Carolina											
Ashe	(Typic Dystrochrept)	A	25.7	3.5	40.9	2.2	147.9	31.1	46.3	3.9	3.8
		Bw	39.9	4.1	5.1	1.1	0.0	50.3	29.5	0.2	1.5
Hayesville	(Typic Hapludult)	Ap	86.9	5.1	11.7	1.2	47.8	24.4	91.3	0.3	2.9
		Bw	292.5	4.7	5.1	0.9	9.9	95.5	117.2	0.1	2.4
Watauga	(Typic Hapludult)	Ap	70.5	6.0	19.6	2.1	231.4	15.6	92.6	32.8	4.6
		Bt_1	194.6	6.4	5.1	0.5	47.4	13.0	165.9	0.1	6.2
South Carolina											
Edneytown	(Typic Hapludult)	A	55.6	3.9	20.8	1.2	43.1	26.1	18.7	0.1	2.1
		E	81.5	4.1	4.7	1.7	0.0	23.3	19.0	0.1	1.1
Tennessee											
Dandridge	(Lithic Ruptic-Alfic Eutrochrept)	A	222.7	4.4	107.1	8.6	524.4	39.2	448.1	65.1	17.1
		E	200.2	3.7	36.3	36.3	202.3	43.7	346.4	37.7	6.6
Dunmore	(Typic Paleudult)	A	58.1	3.6	47.2	3.1	129.6	26.4	73.3	5.6	4.8
		E	97.9	3.9	14.1	1.0	45.7	31.2	42.5	8.1	2.1
Porters	(Umbric Dystrochrept)	A	59.1	3.3	202.3	11.0	915.7	63.3	207.9	35.9	10.2
		Bw	159.9	3.8	16.0	1.2	67.5	89.1	71.0	3.4	4.9
Tate	(Typic Hapludult)	A	93.1	3.9	90.4	3.0	520.4	75.1	472.9	0.1	8.1
		BA	134.9	4.1	57.6	4.8	328.4	101.1	398.7	0.4	5.4
Berks	(Typic Dystrochrept)	A	95.9	3.5	54.8	2.9	212.5	42.3	92.3	0.1	8.4
		E	120.6	3.8	18.1	1.1	40.1	42.9	53.6	0.1	6.4
West Virginia											
DeKalb	(Typic Dystrochrept)	A	50.5	3.9	288.8	14.7	1082.1	97.9	428.1	75.7	10.7
		E	68.4	3.4	40.6	2.3	217.5	40.0	98.6	0.8	6.0
Gilpin	(Typic Hapludult)	A	100.7	5.0	84.6	7.0	500.6	48.9	265.8	1.7	15.6
		BA	124.0	4.8	30.0	2.3	0.0	49.5	166.2	0.1	6.0
Lily	(Typic Hapludult)	A	57.1	3.6	95.8	4.6	338.6	52.9	141.7	13.8	7.0
		BA	105.3	3.7	36.6	1.5	164.3	58.8	77.0	0.1	3.9
Upshur	(Typic Hapludult)	A	218.7	5.0	20.9	1.5	164.3	16.7	123.3	0.1	8.4
		Bt_1	267.8	4.4	10.5	1.0	86.5	22.5	99.6	0.1	11.7
Westmoreland	(Typic Hapludult)	A	67.7	4.2	20.1	1.5	405.5	41.5	266.3	20.2	7.4
		E	103.2	3.9	37.4	3.2	214.3	45.2	204.5	0.1	5.2

[a]CEC = Σ cmol (+) kg^{-1} of (K + Na + Ca + Mg + Al + H).

TABLE 2

Arylsulfatase Activities in Surface (SH) and Subsurface (SSH) Horizons of Appalachian Hill Land Soils.[a]

Soil	Arylsulfatase	
	SH	SSH
Ashe	113hi[b]	37i
Hayesville	197g	72gh
Watauga	413e	31i
Edneytown	67i	30i
Dandridge	909b	333c
Dunmore	354f	99fg
Porters	242g	60hi
Tate	1068a	724a
Berks	129h	95fg
DeKalb	890c	194d
Gilpin	914b	742b
Lily	524d	135e
Upshur	308f	125ef
Westmoreland	417c	217d
Mean	453	187
LSD (0.05)	49	33

[a]Arylsulfatase activity. μg, p-nitrophenol released•g soil^{-1}h^{-1}.
[b]Means within a column not followed by the same letter differ at the 0.05 level of probability by Duncan's New Multiple Range Test.

lishing the level of AS activity. The magnitude of AS activities of subsurface horizons were comparable to those found for Iowa agricultural soils (11,18) and salt marsh soils (12).

Correlation coefficients relating AS activities of surface and subsurface horizons to selected soil properties are shown in Table 3. In the current study, the AS activities were positively related to original moisture by wt. (OMW) ($P < 0.01$) and volume (OMV) ($P<0.05$) and percent water filled pore space (%WFP). Soil moisture is known to have a considerable influence on microbial and enzyme activities of soil (4,14). It has been reported that a decrease in soil moisture content enhanses the magnitude of the measured AS activity (11). However,

TABLE 3

Correlation Coefficients (r) Relating Arylsulfatase Activities and Selected Soil Properties of all (AH), Surface (SH) and Subsurface (SSH) Horizons of Appalachian Soils

Properties	Arylsulfatase AH	SH	SSH
Physical			
Orig. moist wt. (OMW)	0.61**	0.47NS	0.81**
Orig. moist vol. (OMV)	0.45*	0.40NS	0.38NS
WFP %	0.31NS	0.36NS	0.03NS
Clay	-0.03NS	0.33NS	-0.03NS
Sand	-0.04NS	-0.19NS	-0.17NS
Silt	0.07NS	0.12NS	0.22NS
Chemical			
pH - H_2O (pH-H_2O)	0.06NS	0.17NS	-0.11NS
C	0.55**	0.38NS	0.81**
N	0.57**	0.42NS	0.87**
Organic P (OP)	0.84**	0.87**	0.82**
Bray-Ext P (BP)	0.43*	0.25NS	0.17NS
Total S (TS)	0.63**	0.51NS	0.65*
Organic S (OS)	0.63**	0.50NS	0.66**
Extractable S (ES)	0.33NS	0.53NS	0.42NS
Ex Bases (EB)	0.59**	0.65*	0.04NS
CEC	0.65**	0.70**	0.25NS
Mg/(Mg + Ca)	0.59**	0.64*	0.06NS

*, ** Significant at 0.05 and 0.01 levels of probability.
[a]NS = Not significant.

Spier (22) observed a positive relationship between AS activities and soil moisture content in Cook Island (r = 0.45) and Tongan soils (r = 0.82**). Our results are in agreement with Speir's (22) findings. The %WFP is reported to be a good indicator of aerobic and anaerobic microbial activity (14). Overall, we did not observe a significant relation between AS activities and %WFP, probably due to a very narrow range of %WFP values in our soil samples.

In the current study, AS activities were not significantly correlated with clay, sand, and silt content. Tabatabai and Bremner (11) found similar relationships in Iowa agricultural soils. The AS activities did not significantly correlate with soil pH (Table 3). Positive and negative relationships between AS activities and pH have been reported (9,11,22).

The AS activities of both horizons gave a positive relation to C and N content even though the relations were significant only in subsurface soil horizons (Table 3). A direct relationship between AS activities and soil C has been well documented (6,9,11). It is possible that the AS enzyme, like other enzymes, be present as humo-protein complexes being thus protected from microbial decomposition (21,24,25). Enzymes that are capable of bonding to humic matter are known to become resistant to denaturation and proteolysis (20,21). From the present results, it appears that organic C, especially in the subsurface horizons, may play a favorable role in protecting the AS enzyme. The significant correlations between AS activities and soil N content may be an indirect consequence of significant correlation between soil organic C and N.

The AS activities were significantly related to organic P content, while no significant relationships were found with extractable P. Speir (22) has reported positive and negative relationships between AS activities and extractable P in Cook Island and Tongan soils. The AS activities in the current study were positively related to levels of various forms of S in the soil, but significant relations were only observed for organic and total S in subsurface horizons. It has been reported that AS activities have no relationship to total S, and that they are only weakly related to inorganic S (4,11). Positive (5,22) and negative (22) relations between AS activities and adsorbed S have been reported for various soil types. The AS activities were significantly related to CEC, exchangeable bases and Mg/(Mg + Ca) only in surface horizons.

CONCLUSIONS

The observed enzyme activities were significantly related to organic C content of the soils. From these results it would appear that crop production in these soils is highly dependent upon the conservation of organically rich surface soil because most of the nutrients for plant growth are in this layer mainly in organic forms. Retention of organic C in soil layers is essential because humic colloids can protect the enzymes from denaturation and proteolysis by forming humic-enzyme complexes. The determination of the magnitude of enzyme activities and the evaluation of relationships between enzyme activities and soil constituents appears to be a good approach for the judicial fertility management of hill-land soils.

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